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ANALYSIS IN TERMS OF THE WILSON, NRTL (NON RANDON TWO LIQUIDS) AND UNIQUAC MODELS OF THE EXPERIMENTAL VAPOR - LIQUID EQUILIBRIUM DATA IN BINARY AND TERNARY SYSTEMS CONTAINING {(1*R,*4*S*)-(+)-FENCHONE, METHYL CHAVICOL AND *TRANS*-ANETHOLE}

IOAN BÂTIU[a]

ABSTRACT. The experimental vapor-liquid equilibrium data (VLE) in binary and ternary systems containing {(1R,4S)-(+)-fenchone, methyl chavicol and trans-anethole}, reported in previous papers, were correlated by means of Wilson, NRTL and UNIQUAC equation. The binary parameters of the corresponding models were calculated. The Wilson, NRTL and UNIQUAC parameters obtained from the isobaric T-x-y measurements at P=4000 Pa in binary systems were used to calculate the VLE data in the ternary system at the same pressure. A comparison with the experimental VLE data was done. The accuracy of the correlation is satisfactory. The Wilson, NRTL (Non Randon Two Liquids) and UNIQUAC models are the most useful models to correlate the experimental vapor – liquid equilibrium data.

Keywords: *Vapor - liquid equilibria, Terpenoids, Wilson, NRTL, UNIQUAC.*

INTRODUCTION

(1*R,*4*S*)-(+)-Fenchone [(1*R,*4*S*)-(+)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-one], methyl chavicol [4-allyl-1-methoxybenzene] and *trans*-anethole [*trans*-1-methoxy-4(prop-1-en-1-yl) benzene] are the main components of the essential oil from the fruits of bitter fennel (*Foeniculum vulgare Mill, fam. Umbelliferae*). Both the raw essential oils and its isolated pure components are used in perfumery, cosmetics, pharmacy, aromatherapy and food industry [1].

Generally, essential oil components belong to the terpenoid class. Terpenoids are natural products comprising a large number of compounds with complicate chemical structures. Many essential oil components are monoterpenoids (C_{10}) and sesquiterpenoids (C_{15}), acyclic, monocyclic or bicyclic, saturated or unsaturated.

Batch distillation is an important unit operation frequently used for small scale production. Batch distillation is preferably to continuous distillation when small quantities of high value added chemicals and biochemicals need to separate. The main components of the essential oil are high value added chemicals.

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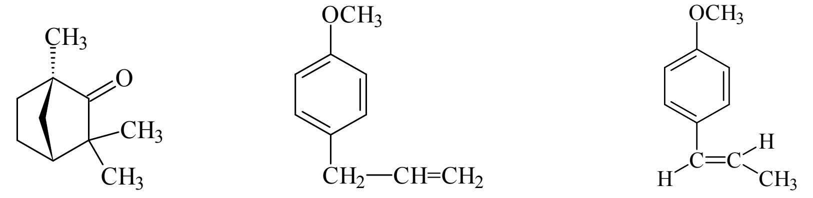
[a] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. Kogălniceanu, Nr. 1, RO-400084 Cluj-Napoca, Romania, batiu@chem.ubbcluj.ro*

There are two basic mode of operating batch distillation column: constant reflux ration and variable product composition, respectively variable reflux ratio and constant key component composition. Also, there is the third mode of operation where neither the reflux ratio no the product composition is kept constant. This type of operation is possible in batch distillation and is known as the optimal reflux or the optimal control policy [2].

The second mode of operation is used to obtain the keys components of high purity. The main components separate function of their boiling points. The first key component distils at the lower temperature than the second key component. The third component distils at the higher temperature than the second key component. To reduce the energy consumes in the reboiler and to eliminate degradation of the key components it is necessary to adjust the pressure inside the batch distillation column.

Accurate isobaric vapor-liquid equilibrium data are necessary for the design and optimization of the batch distillation column. The literature [3, 4] is very poor in the vapor - liquid equilibrium data in the field of terpenoids.

The chemical structures of the main components of the essential oils of fennel are presented in Figure 1. The names of the components referred to in this paper are: (+)-fenchone, methyl chavicol and *trans*-anethole.



(1*R*,4*S*)-(+)-Fenchone Methyl chavicol t*rans*-Anethole

Figure 1. Chemical structure of (1*R*,4*S*)-(+)-fenchone, methyl chavicol and *trans*-anethole

RESULTS AND DISCUSSIONS

In the binary systems containing **{**(+)-fenchone, methyl chavicol and *trans*-anethole} the values of the experimental activity coefficients, γ_i are ranging from ca. 0.75 to ca. 1.08. The experimental fugacity coefficients, φ_i are very close to unity [5]. This means that a quasi-ideal behavior of the liquid phase and ideal behavior of the vapor phase can be considered.

Reduction of the experimental VLE data by non-electrolyte solutions models

The experimental VLE data of the all binary systems have been correlated by means of the Wilson [6], NRTL [7, 8] and UNIQUAC [9] activity coefficient, γ_i equations (eq. 1- 12).

The Wilson equations:

$$\ln\gamma_1 = -\ln\left(x_1 + \Lambda_{12}x_2\right) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{1}$$

$$\ln\gamma_2 = -\ln\left(x_2 + \Lambda_{21}x_1\right) - x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \tag{2}$$

$$\Lambda_{12} = \frac{V_2^L}{V_1^L}\exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) \qquad \Lambda_{21} = \frac{V_1^L}{V_2^L}\exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right) \tag{3}$$

where: γ_i is the activity coefficient of component *i*; x_i is the mole fraction of component *i*; in the liquid phase, V_i^L is the molar volume of component *i;* $(\Lambda_{12}, \Lambda_{21})$ and $\left[(\lambda_{12} - \lambda_{11}), (\lambda_{21} - \lambda_{22})\right]$ are two adjustable parameters of the Wilson model.

The NRTL equations

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \left(\frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right)\right] \tag{4}$$

$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \left(\frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right)\right] \tag{5}$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT}; \tau_{21} = \frac{g_{21} - g_{11}}{RT}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}); a_{ij} = (g_{ij} - g_{jj}); \alpha_{ij} = \alpha_{ji} \tag{6}$$

where: γ_i is the activity coefficient of component *i*; x_i is the mole fraction of component *i*; in the liquid phase, (τ_{12}, τ_{21}) and $\left[(g_{12} - g_{22}), (g_{21} - g_{11})\right]$ are two adjustable parameters of the NRTL model; *α* is the third parameter of the NRTL model.

The UNIQUAC equations

The activity coefficient, γ_i is calculated as the sum of two terms (eq. 7):

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \tag{7}$$

where: the combinatorial part ($\ln\gamma_i^C$) accounts for entropic effects, while the residual part (γ_i^R) describes the interactions between the different groups from molecule. For a binary system:

$$\ln\gamma_1^{\ C} = \ln\frac{\phi_1}{x_1} + \left(\frac{z}{2}\right)q_1 \ln\frac{\theta_1}{\phi_1} + \phi_2\left(l_1 - \frac{r_1}{r_2}l_2\right) \tag{8}$$

$$\ln\gamma_2^{\ C} = \ln\frac{\phi_2}{x_2} + \left(\frac{z}{2}\right)q_2 \ln\frac{\theta_2}{\phi_2} + \phi_1\left(l_2 - \frac{r_2}{r_1}l_1\right) \tag{9}$$

$$\ln\gamma_1^{\ R} = -q_1\ln\left(\theta_1 + \theta_2\tau_{21}\right) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}}\right) \tag{10}$$

$$\ln\gamma_2^{\ R} = -q_2\ln\left(\theta_1\tau_{12} + \theta_2\right) + \theta_1 q_2\left(\frac{\tau_{12}}{\theta_1\tau_{12} + \theta_2} - \frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}}\right) \tag{11}$$

$$\tau_{21} = \exp\left(-\frac{u_{21} - u_{11}}{RT}\right); \tau_{12} = \left(-\frac{u_{12} - u_{22}}{RT}\right)$$

$$l_1 = \left(\frac{z}{2}\right)\left(r_1 - q_1\right) - \left(r_1 - 1\right); l_2 = \left(\frac{z}{2}\right)\left(r_2 - q_2\right) - \left(r_2 - 1\right); z = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; i = 1{,}2 \qquad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}; i = 1{,}2 \tag{12}$$

where: x_i is the mole fraction of component *i*; in the liquid phase, θ_i is the area fraction of component *i*; Φ_i is the segment fraction of component *i* which is similar to volume fraction. Pure component parameters *r,* and q_i are measures of molecular van der Waals volumes and molecular surface area, respectively; (τ_{12}, τ_{21}) and $\left[\left(u_{12} - u_{22}\right), \left(u_{21} - u_{11}\right)\right]$ are two adjustable parameters of the UNIQUAC model.

The Wilson, NRTL and UNIQUAC adjustable parameters must be evaluated from experimental vapor-liquid equilibrium data. They are used to calculate vapor-liquid equilibrium data at other pressures than those from which were calculated. The pressure inside the batch distillation column is chosen taking into consideration the boiling points of the key components which successively separate at the top of the batch distillation column. Due to the high boiling points of the terpenoids the pressures inside the batch distillation column are adjusted at values smaller than the atmospheric pressure.

The Wilson, NRTL and UNIQUAC binary parameters were calculated from the isobaric *T-x-y* measurements and from the *T-P-x* measurements performed at the constant liquid phase compositions, x_i, respectively by minimizing the following objective functions (***S***):

- the maximum likelihood multimodel fitting method [10] (eq. 13)

$$S = \sum_{i=1}^{N} \left[(P_{ie} - P_{ic})^2 / \sigma_P^2 + (T_{ie} - T_{ic})^2 / \sigma_T^2 + (x_{ie} - x_{ic})^2 / \sigma_x^2 + (y_{ie} - y_{ic})^2 / \sigma_y^2 \right] \quad (13)$$

where: N is the number of experimental points, P_{ie}, T_{ie}, x_{ie} and y_{ie} are the experimental data and P_{ic}, T_{ic}, x_{ic} and y_{ic} are the corresponding calculated values for pressure, temperature, and the liquid and vapor phase compositions, respectively. In this paper, the standard deviation for pressure, temperature, and liquid and vapor phase compositions were set to σ_P = 60 Pa, σ_T = 0.05 K, σ_x = 0.003 mol. fr. and σ_y = 0.003 mol. fr., respectively.

- the boiling points condition, eq. (14):

$$S = \sum_{i=1}^{N} [1 - (P_1^0 / P) x_1 \gamma_1 (A_{12}, A_{21}) - (P_2^0 / P) x_2 \gamma_2 (A_{12}, A_{21})]_i = \min . \quad (14)$$

where: N is the number of experimental points, P is the total pressure, P_1^0 and P_2^0 are the vapor pressures of the pure components 1 and 2, A_{12} and A_{21} are, respectively, the binary parameters of the Wilson, NRTL and UNIQUAC models, γ_1 and γ_2 are the activity coefficients, x_1 and x_2 are the mole fractions of the pure components 1 and 2 in the liquid phase.

The purport of the calculated binary parameters, A_{12} and A_{21} (eq. 14) is: $[\Lambda_{12}, \Lambda_{21}]$ (Wilson); $[\tau_{12}, \tau_{21}]$ (NRTL) and $[(u_{12} - u_{22}), (u_{21} - u_{11})]$ (UNIQUAC), respectively B_{12} and B_{21} (eq. 13): $[(\lambda_{12} - \lambda_{11}), (\lambda_{21} - \lambda_{22})]$ (Wilson); $[(g_{12} - g_{22})$, $(g_{21} - g_{11})]$ (NRTL) and $[(u_{12} - u_{22}) / R, (u_{21} - u_{11}) / R]$ (UNIQUAC).

The binary parameters of each model (A_{12}, A_{21}, respectively B_{12}, B_{21}), the statistic criterion of the all experimental points (*global Ro*), the absolute mean deviations in the vapor phase compositions, *AMD(y)/*mol. fr. and in pressure, *AMD(P)*/Pa are reported in Tables 1 - 3.

It should be noted that the values of the binary parameters of the Wilson, NRTL and UNIQUAC models, for the same isobaric *T-x-y* measurements, are not identical when the two objective functions are used. Using the same objective function - the boiling points condition – the calculated binary parameters from the isobaric *T-x-y* measurements and from *T-P-x* measurements are different. This fact do not affect the VLE prediction if the binary parameters are used only to calculate VLE data at the same pressure or at others pressures. Consequently, the vapor phase compositions, y_i/mol. fr. at the pressure of P=4000 Pa and, respectively P=4270 Pa, calculated using the Wilson, NRTL and UNIQUAC binary parameters obtained from our P-T-x_i experimental data, are in good agreement with our P-T-x_i-y_i experimental data (Table 4). The absolute mean deviations, *AMD(y)* and *AMD(P)* for all the binary systems are less than 0.01 mol. fr. and respectively 100 Pa.

Table 1. Binary parameters of the Wilson, NRTL (α = 0.3) and UNIQUAC models for the binary systems containing (+)-fenchone, methyl chavicol and *trans*-anethole obtained from isobaric VLE data *T-x-y* (the object function - the maximum likelihood multimodel fitting method).

	Models								
	Wilson			NRTL (α=0.3)			UNIQUAC		
Systems/Pressure	B_{12}(*A_{12})	B_{21}(*A_{21})	Ro	B_{12}(*A_{12})	B_{21}(*A_{21})	Ro	B_{12}(*A_{12})	B_{21}(*A_{21})	Ro
(+)-fenchone (1) + methyl chavicol (2)/ *P*=4000 Pa	-136.29 *1.0198	-143.99 *1.0725	0.804	-144.11 *1.0471	*-142.88 *1.0467	0.804	-3.784 *-31.412	-3.690 *-30.664	0.804
(+)-fenchone (1) + methyl chavicol (2)// *P*=4270 Pa	3421.28 *0.3286	-2021.48 *1.9492	0.712	21.18 0.9932	24.17 *0.9923	0.799	0.395 *3.3240	0.543 *4.4874	0.798
(+)-fenchone (1) + *trans* anethole (2)/ *P*=4000 Pa	494.65 *0.8439	-506.98 *1.189	1.003	-905.28 *1.329	879.79 *0.7585	1.006	-1.396 *-11.634	-1.174 *-9.7227	1.006
methyl chavicol (1) + *trans* anethole (2)/ *P*=4000 Pa	-1454.95 *1.5695	2272.61 *0.4972	0.783	3260.34 *1.73669	-2247.87 *-0.8728	0.769	4.022 *33.4062	4.039 *33.5724	0.803

Ro - the statistic criterion of the all experimental points (*global Ro*), B_{12}, B_{21} - Wilson [$(\lambda_{12}-\lambda_{11})$, $(\lambda_{21}-\lambda_{22})$] and NRTL [$(g_{12}-g_{22})$, $(g_{21}-g_{11})$] parameters unit $\mathrm{Jmol^{-1}}$;UNIQUAC [$(u_{12}-u_{22})/R$,$(u_{21}-u_{11})/R$] parameter unit K; *A_{12}, *A_{21} – Wilson and NRTL dimensionless parameters; UNIQUAC parameter unit $\mathrm{Jmol^{-1}}$.

Table 2. Binary parameters of the Wilson, NRTL (α = 0.3) and UNIQUAC models for the binary systems containing (+)-fenchone, methyl chavicol and *trans*-anethole obtained from isobaric VLE data *T-x-y* (the object function - the boiling points condition).

	Models								
	Wilson			NRTL (α=0.3)			UNIQUAC		
Systems/Pressure	A_{12}	A_{21} *AMD(P)*	*AMD(y)/*	A_{12}	A_{21} *AMD(P)*	*AMD(y)/*	A_{12}	A_{21} *AMD(P)*	*AMD(y)*
(+)-fenchone (1) + methyl chavicol (2)/ *P*=4000 Pa	1.3514	0.7041	01/ 45	-0.1946	0.2002	0.01/ 44	4.00	2.00	0.01/ 70
(+)-fenchone (1) + methyl chavicol (2)/ *P*=4270 Pa	0.1408	2.4010	0.0096/ 60	-1.1400	1.9458	0.0098/ 56	5.00	10.00	0.0089/ 100
(+)-fenchone (1) + *trans* anethole (2)/ *P*=4000 Pa	0.7713	1.3107	0.0066/ 71	0.1066	-0.1470	0.0067/ 72	1.00	0.50	0.0095/ 90
methyl chavicol (1) + *trans* anethole (2)/ *P*=4000 Pa	2.0602	0.2088	0.01/ 25	1.6781	-0.9667	0.01/ 26	5.00	1.00	0.002/ 117

Absolute mean deviations in the vapor phase composition, *AMD(y)*/mol. fr. and in pressure, *AMD(P)*/Pa, UNIQUAC parameter unit Jmol^{-1}.

Table 3. Binary parameters of the Wilson and NRTL (α = 0.3) and UNIQUAC models for the binary systems containing, (+)-fenchone, methyl chavicol and *trans*-anethole obtained from VLE data *T-P-x* (the object function - the boiling points condition)

	Models								
	Wilson			NRTL (α=0.3)			UNIQUAC		
Systems/Pressure	A_{12}	A_{21}	*AMD(P)*	A_{12}	A_{21}	*AMD(P)*	A_{12}	A_{21}	*AMD(P)*
(+)-fenchone (1) + methyl chavicol (2)	0.9898	1.0133	49	-0.6476	0.80038	53	0.50	1.00	57
(+)-fenchone (1) + *trans* anethole (2)	0.6707	1.5108	57	-0.5585	0.5574	58	-5.616	-7.955	54
methyl chavicol (1) + *trans* anethole (2)	2.1743	0.1585	40	19.258	20.2157	53	19.00	10.00	57

Absolute mean deviations in in pressure, *AMD(P)*/Pa, UNIQUAC parameter unit Jmol^{-1}.

Table 4. Comparison between experimental isobaric VLE data, *T-x-y* and calculated isobaric VLE data, *T-x-y* using the binary parameters of the Wilson, NRTL (α=0.3) and UNIQUAC models obtained from *T-P-x* measurements. Binary systems: (+)-fenchone + methyl chavicol (*P*=4000 Pa and, respectively *P*=4270 Pa*), (+)-fenchone + *trans*-anethole (*P*=4000 Pa) and methyl chavicol + *trans*-anethole (*P*=4000 Pa).

Models/Binary systems	*AMD(y)/*mol. fr.	*AMD(P)*/Pa
Wilson		
(+)-fenchone + methyl chavicol	0.010	45.00
*(+)-fenchone + methyl chavicol	0.005	100.00
(+)-fenchone + *trans*-anethole	0.009	78.00
methyl chavicol + *trans*-anethole	0.010	30.00
NRTL		
(+)-fenchone + methyl chavicol	0.010	45.00
*(+)-fenchone + methyl chavicol	0.004	100.00
(+)-fenchone + *trans*-anethole	0.009	80.00
methyl chavicol + *trans*-anethole	0.003	70.00
UNIQUAC		
(+)-fenchone + methyl chavicol	0.010	50.00
*(+)-fenchone + methyl chavicol	0.005	97.00
(+)-fenchone + *trans*-anethole	0.009	90.00
methyl chavicol + *trans*-anethole	0.010	60.00

AMD(y)/mol.fr. - Absolute mean deviations in the vapor phase*;* *AMD(P)*/Pa - Absolute mean deviations in pressure.

Calculated VLE data in the ternary system (+)-fenchone + methyl chavicol + trans-anethole using the binary parameters of the Wilson, NRTL and UNIQUAC models

The binary parameters of the Wilson, NRTL and UNIQUAC models, calculated from isobaric *T-x-y* data at *P*=4000 Pa, using the objective function (*S*) (eq. 13) - the maximum likelihood multimodel fitting method – have been used to calculate VLE data in the ternary system {(+)-fenchone + methyl chavicol + *trans*-anethole} (Table 5). The absolute mean deviations in the vapor phase composition, *AMD*(*y*)/mol.fr. are practicaly the same for all the models, while absolute mean deviation in temperature, *AMD*(*T*)/K exhibits rather small differences. We appreciate that, due to the same deviations in the vapor phase compositions and due to the small deviations in the temperature, the binary parameters of the Wilson, NRTL and UNIQUAC models present the same accuracy in calculating the vapor liquid equilibrium data.

In a previous paper [11] we checked the predictive capability of the neuronal networks in the ternary system {(+)-fenchone + methyl chavicol + *trans*-anethole}. The vapor phase compositions, y_i were calculated after training the network considering the experimental liquid phase compositions, x_i of all the binary systems as inputs in each neuronal networks. The calculated vapor phase compositions, $y_{i,c}$ were compared with experimental vapor phase compositions, $y_{i,exp}$ at the liquid phase compositions, x_i of the ternary system. The absolute mean deviation in the vapor phase composition, $AMD(y)$ was 0.01 mol. fr. (not calculated in paper) proving the better predictive capability of the VLE data using the neuronal network.

Table 5. Comparison between experimental isobaric VLE data *T-x-y* of the ternary system (+)-fenchone + methyl chavicol + *trans*-anethole and calculated isobaric VLE data *T-x-y* data using the binary parameters of the Wilson, NRTL (α=0.3) and UNIQUAC models obtained from the isobaric VLE data *T-x-y* of the binary systems at *P*=4000 Pa (objective function - the maximum likelihood multimodel fitting method).

Ternary system/Model	*AMD(y)/*mol. fr.	*AMD(T)*/K
(+)-fenchone + methyl chavicol + *trans*-anethole/		
Wilson	0.023	1.29
NRTL (α=0.3)	0.023	1.37
UNIQUAC	0.022	1.13

AMD(y)/mol.fr. - Absolute mean deviation in the vapor phase*;*
AMD(T)/K- Absolute mean deviation in temperature.

CONCLUSION

We have presented and correlated the experimental vapor-liquid equilibrium data (VLE) in binary and ternary systems containing **{**(1R,4S)**-**(+)-fenchone, methyl chavicol and trans-anethole} by means of Wilson, NRTL and UNIQUAC equation. The binary parameters of the corresponding models were calculated. The Wilson, NRTL and UNIQUAC parameters obtained from the isobaric *T-x-y* measurements at *P*=4000 Pa in systems which contain {(+)-fenchone, methyl chavicole and *trans*-anethole} were used to calculate the VLE data in the ternary system {(+)-fenchone + methyl chavicole + *trans*-anethole}. The calculated VLE data was compared with experimental VLE data. The accuracy is satisfactory.

EXPERIMENTAL SECTION

In previous papers [12, 13, 14] we reported experimental vapor-liquid equilibrium data for the following binary and ternary systems: {(+)-fenchone (1) + methyl chavicol (2)}; {(+)-fenchone (1) + *trans*-anethole (2)}; {methyl chavicol (1) + *trans*-anethole (2)}; {(+)-fenchone (1) + methyl chavicol(2) + *trans*-anethole (3)}.

A series of isobaric *T-x-y* measurements were performed at (4000±30) Pa [12, 13, 14]. Another series of *T-P-x* measurements were performed at three constant liquid-phase compositions [12, 13]. For the binary system (+)-fenchone (1) + methyl chavicol (2) a series of isobaric *T-x-y* measurements were performed at (4270±30) Pa [12].

VLE data in binary systems were found to be thermodynamically consistent as tested by using the maximum likelihood multimodel fitting method described by Panaitescu [10]. The thermodynamic consistency of the isobaric *T-x-y* measurements in the ternary system was checked using the McDermott-Ellis method [15] modified by Wisniak and Tamir [16].

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